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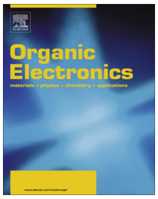

Solution-based 5,6,11,12-tetrachlorotetracene crystal growth for high-performance organic thin film transistors

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ABSTRACT

5,6,11,12-Tetrachlorotetracene is a *p*-type semiconductor with high hole mobility due to its face-to-face molecular packing and improved electronic coupling. In this study, we demonstrate for the first time the solution processing of 5,6,11,12-tetrachlorotetracene with crystal alignment for the application of organic thin film transistors (OTFTs). Enhanced crystal orientation is achieved by confining the solvent evaporation in a restricted space, which introduces a capillary force and effectively aligns the 5,6,11,12-tetrachlorotetracene crystals. At the same time, a double solvent approach (chloroform/methanol) is utilized to tune the crystal size. The addition of polar hydroxyl groups from methanol weakens the interaction between the less polar 5,6,11,12-tetrachlorotetracene solutes and chloroform solvent, and leads to the formation of supramolecular aggregation. The aggregation acts as nucleation seeds for the crystallization of 5,6,11,12-tetrachlorotetracene semiconductor with enlarged crystal width. As a result, the 5,6,11,12-tetrachlorotetracene based OTFTs demonstrate a maximum hole mobility of 1.1 cm^2/Vs, which is the highest value ever reported from the solution-processed OTFTs based on 5,6,11,12-tetrachlorotetracene semiconductor.

1. Introduction

Organic semiconductors have attracted considerable attention due to their compatibility with solution-based and low-temperature processing techniques, which open up the application possibilities of inexpensive and large-area flexible electronics [1–4]. 5,6,11,12-Tetrachlorotetracene, as a derivative of tetracene, exhibits significantly improved charge transport, due to its face-to-face packing motif and greatly enhanced π–π orbital overlap [5]. This property makes it a promising candidate for the active layer of *p*-type organic thin film transistors (OTFTs) [6].

Chi et al. reported the first 5,6,11,12-tetrachlorotetracene single crystal field-effect transistor with a mobility up to 1.7 cm^2/Vs [7]. Subsequently, Yagodkin et al. demonstrated 5,6,11,12-tetrachlorotetracene single crystal field-effect transistor on a PDMS substrate, and their reported mobility was 0.2 cm^2/Vs [5]. In both cases, crystals were grown by the vapor phase deposition, which requires high temperature and high vacuum, and therefore is not suitable for inexpensive and large-area manufacturing of flexible electronics [8]. It is possible, however, that this material could be utilized to fabricate OTFTs based on solution-processing techniques, since 5,6,11,12-tetrachlorotetracene has a reasonably good solubility in organic solvents. With solution processing methods, such as drop casting, 5,6,11,12-tetrachlorotetracene tends to form crystals with random orientation, which usually leads to anisotropic charge transport and large device-to-device performance variations [9]. Thus, it is important that crystals are well aligned. In particular, when the bottom-contact OTFT configuration is used, controlled crystal growth from source to drain electrodes is imperative in order to maximize charge transport and maintain performance consistency of OTFTs [10].

In this study, we demonstrate for the first time the solution-processed 5,6,11,12-tetrachlorotetracene crystals with improved alignment for the fabrication of OTFTs. Since simple drop casting of 5,6,11,12-tetrachlorotetracene solution results in multiple layers of randomly-orientated crystals stacking upon each other, a particular method was utilized here to align the randomly oriented crystals by controlling the solvent evaporation in a restricted space. At the same time, double solvents were used for tuning the crystal size with the aim to increase the crystal width. As a result, 5,6,11,12-tetrachlorotetracene crystals formed in double solvents with controlled solvent evaporation exhibit preferential orientation from source to drain, which leads to a maximum hole mobility of 1.1 cm^2/Vs when a bottom-gate, bottom-contact OTFT configuration is used. The uniform crystal orientation

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simultaneously contributes to a significant enhancement of performance consistency of OTFTs.

2. Experiment

5,6,11,12-Tetrachlorotetracene was synthesized based on a previously reported procedure [11]. 5,6,11,12-Tetrachlorotetracene was firstly dissolved in "good" solvent chloroform at a concentration of 3 mg/mL, before being injected into "bad" solvent methanol at different ratios. The crystals were formed by drop casting 5,6,11,12-tetrachlorotetracene in chloroform/methanol double solvents onto SiO_2 substrate in a solvent annealing environment. Controlled solvent evaporation and crystal alignment were achieved by confining the solution in a restricted space. Optical micrographs of 5,6,11,12-tetrachlorotetracene thin films were taken using a Zeiss Axioplan optical microscope with a built-in camera. X-ray diffraction (XRD) spectra of the thin films were measured using a Philips X'Pert X-ray diffractometer.

Bottom-gate, bottom-contact OTFTs were fabricated to examine the charge transport in the well-aligned 5,6,11,12-tetrachlorotetracene microribbons. Gold contacts were patterned onto the heavily-doped *n*-type silicon substrate with a 250 nm thermal oxide via photolithography, metal deposition and lift-off. Prior to the formation of active layer, surface treatments were carried out including both hexamethyldisilazane (HMDS) and pentafluorobenzenethiol (PFBT) treatment [12]. In specific, the gate dielectric was modified with HMDS self-assembled monolayers formed via vapor deposition at 140 °C for 30 min, followed by rinsing with isopropanol. The HMDS treatment can effectively passivate the silanol groups on the hydrophilic SiO_2 surface, since such silanol groups may serve as charge trap centers and degrade device performance. The source/drain contacts were modified with PFBT treatment by immersing the substrates in a PFBT/toluene solution at a concentration of 10 mM for 2 h, and rinsing them with toluene. The PFBT treatment was used to increase the work function of the Au electrodes, which reduces the energy barrier for hole injection from electrode to *p*-type 5,6,11,12-tetrachlorotetracene semiconductor. Electrical characterization was performed by using an Agilent B1500A semiconductor parameter analyzer. All measurements were carried out at room temperature in ambient environment. Field-effect mobility in the saturation regime was extracted from the slope of the transfer characteristic $(I_{DS})^{1/2} - V_{GS}$.

3. Results and discussion

The molecular structure of 5,6,11,12-tetrachlorotetracene is shown in Fig. 1(a). It is well known that polyacenes, including tetracene, adopt the herringbone packing pattern with an edge-to-face arrangement, where the π–π orbital overlap is not maximized [13,14]. In contrast, 5,6,11,12-tetrachlorotetracene with the chlorine side groups added to the tetracene backbone forms a face-to-face stacking pattern. This type of packing structure has been shown to enhance the π–π orbital overlap and significantly improve the hole mobility [7]. When it is drop casted from chloroform onto the substrate, the resultant 5,6,11,12-tetrachlorotetracene film exhibits a few layers of crystals stacking over each other. Each layer is composed of multiple randomly oriented, grass-like crystals, as shown in Fig. 1(b).

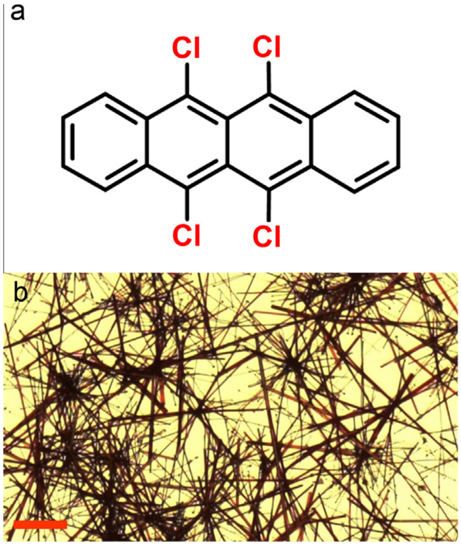

Fig. 1. (a) Molecular structure of 5,6,11,12-tetrachlorotetracene. (b) Film morphology of 5,6,11,12-tetrachlorotetracene crystals when drop casted from pure chloroform without applying the controlled solvent evaporation method. The scale bar in (b) represents 100 microns.

In order to obtain uniformly aligned crystals, the solvent evaporation is controlled in a restricted space. Similar approaches have been previously demonstrated to achieve crystal growth with effective alignment. For example, Han et al. demonstrated the "controlled evaporative self-assembly (CESA)" method to achieve well-ordered structures of conjugated polymers [15]. Diao and coworkers reported the "fluid-enhanced crystal engineering (FLUENCE)" approach to control the morphology of solution-printed thin films, and achieved a high degree of crystal alignment [16]. Our method of controlled solvent evaporation in restricted space is illustrated in Fig. 2. A glass cylinder is placed onto the substrate (Fig. 2(a)), and a capillary force is introduced at the close proximity between the glass cylinder and substrate [17]. The direction of the capillary force is represented by the black arrows, normal to the contact center between cylinder and substrate, as shown in Fig. 2(b). This capillary force along with the pinning force [18] confines the solution within the restricted space and impacts the crystallization of 5,6,11,12-tetrachlorotetracene. As the solvent evaporates, the contact angle reduces and so does the pinning force. When the pinning force continues to decrease to a point where it's smaller than the capillary force, the capillary force attracts the solution toward the close proximity between the glass cylinder and the substrate, facilitating the contact line to move forward. In the meanwhile, as the solvent evaporates, the 5,6,11,12-tetrachlorotetracene solute concentration increases, resulting in crystal growth along the direction of the capillary force. As a result, the controlled solvent evaporation method navigates the 5,6,11,12-tetrachlorotetracene crystal growth and improves its crystal orientation in the preferential direction from source to drain contacts (Fig. 2(c)).

Fig. 3(a) shows the morphology of 5,6,11,12-tetrachlorotetracene crystals drop casted from pure chloroform solvent with application of the controlled solvent evaporation. Although the controlled solvent evaporation method shows some alignment effect, the crystal misorientation still persists and small crystals with large gaps dominate. To further address these issues, the double solvent scheme was applied along with the controlled solvent evaporation. Based on their solubility, 1,4-dichlorobenzene, toluene and chloroform could be "good" solvents, whereas methanol was used as a "bad" solvent because the 5,6,11,12-tetrachlorotetracene solute can be barely dissolved in methanol. In addition to solubility, the boiling points of the good and bad solvent should be close to each other to ensure simultaneous evaporation. The boiling points of 1,4-dichlorobenzene (180.5 °C) and toluene (110.6 °C) are much higher than that of methanol (64.7 °C), while only chloroform has a boiling point (61.2 °C) close to that of methanol. Therefore, by considering the criteria of both solubility and boiling point, the mixture of chloroform/methanol